Noncontact electrical characterization of low-resistivity p-type ZnSe:N grown by molecular beam epitaxy

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The resistivity of p-type ZnSe:N/GaAs heteroepitaxial layers grown by molecular beam epitaxy using a nitrogen free-radical source has been determined as a function of both substrate temperature and the Zn-to-Se beam equivalent pressure (BEP) ratio employed during growth. Layer resistivities were determined using a noncontact inductive-coupling radio-frequency measurement technique that provided sheet conductivity data from which layer resistivities were calculated. A minimum resistivity of 0.75 Ω cm has been measured to date for p-type ZnSe:N material grown at 235 °C with a BEP ratio of 1:2. Such a resistivity would imply a free-hole density in the range 4×10^{17}–8×10^{17} cm^{-3} assuming the hole mobility to be in the range 20–10 cm^2 V^{-1} s^{-1}, respectively.

Research efforts, at present, concerning the wide band-gap II-VI compound semiconductor ZnSe ($E_g \simeq 2.7$ eV at RT), are primarily focused on developing the material in order that short-wavelength ZnSe light-emitting devices [light emitting diodes (LEDs) and diode lasers] can be fabricated. Of particular concern over the last decade has been the apparent difficulties associated with the provision of stable, low-resistivity p-type ZnSe epitaxial material which is a required ingredient for the fabrication of the above-mentioned optoelectronic devices. However, recent publications that have reported epitaxial growth of low-resistivity p-type ZnSe by nitrogen doping using both molecular beam epitaxy (MBE) and metalorganic molecular beam epitaxy (MO-MBE) techniques are extremely encouraging in this respect.

In terms of MBE growth, Park et al.[1] recently reported using a nitrogen free-radical source, which provides a flux of highly reactive atomic nitrogen species, to grow ZnSe:N material having net acceptor concentrations, as determined by capacitance-voltage (C-V) measurements, in the 10^{17} cm^{-3} range. Ohkawa, Karasawa, and Mitsuya[2] have also employed a nitrogen free-radical source to grow p-type ZnSe:N by MBE although these authors reported lower acceptor densities, in the 10^{15} cm^{-3} range, for their material. MO-MBE growth of low-resistivity ZnSe:N material has also recently been reported by Taike, Migita, and Yamamoto[3] using NH$_3$ as the source of N. These authors report measuring carrier densities as high as 5.6×10^{17} cm^{-3} with resistivities as low as 0.57 Ω cm.

The above-mentioned results are particularly encouraging since N has long been considered to be a good candidate dopant for the provision of stable, low-resistivity p-type ZnSe.[4] Moreover, Chadi and Chang[5] in their more recent theoretical paper suggested that N would be a good candidate dopant (at least more appropriate than As or P) based on their self-compensation through lattice relaxation model.

The purpose of the present letter is to report on the growth parameter dependence of the resistivity of p-type

ZnSe:N material grown by MBE using a nitrogen free-radical source.

ZnSe:N layers having thicknesses in the 1–2 μm range were grown by MBE at the University of Florida on GaAs substrates using a variety of substrate temperatures and Zn-to-Se beam equivalent pressure (BEP) ratios. N was efficiently incorporated into the ZnSe layers during growth using a nitrogen free-radical source as described in Ref. 1. The plasma discharge intensity in the free-radical source and, therefore, the concentration of N atoms in the plasma, was maintained at the same level for each growth run.

Since serious problems currently exist with regard to providing low-resistance ohmic contact to p-type ZnSe material (see, for example, Ref. 6), a noncontact electrical measurement technique was employed in this work to determine sample resistivities as opposed to the more conventional Hall-effect measurement approach which requires low-resistance ohmic contacts for accurate determination of sample resistivity. It should be noted that Ohkawa and co-workers[2] reported achieving an order of magnitude reduction in contact resistance to their p-type ZnSe:N material employing Pt electrodes compared with more traditional Au electrodes, the Pt electrodes being sputter deposited on an Ar plasma-etched surface. However, although these authors were able to perform Hall-effect measurements on their ZnSe:N material using Pt electrodes, they note in their publication that the Pt electrodes showed Schottky rather than ohmic behavior, which they speculate is due to a Fermi level offset.

The apparatus shown in Fig. 1 was used to measure the sheet conductivity of the doped ZnSe layers by radio-frequency (rf) inductive coupling.[7] The apparatus is essentially identical to the contactless minority-carrier lifetime probe of Ref. 7, except that in this work steady-state conductivity, rather than pulsed conductivity, was measured. In the arrangement shown in Fig. 1, the doped epilayer acts as a one-turn secondary, inductively coupled to a five-turn primary coil operating at 500 MHz. The reflected radio signal from the primary is directly proportional to
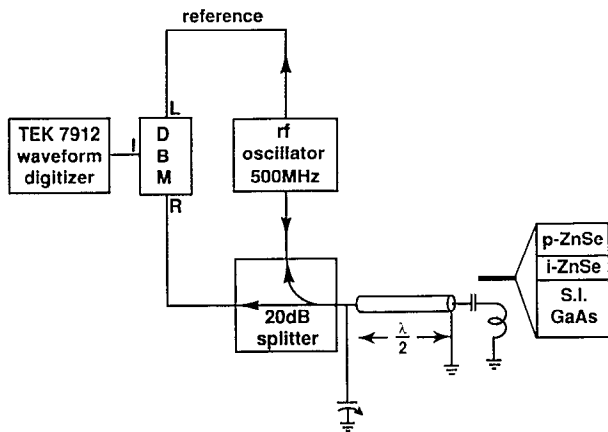
FIG. 1. Sheet conductance of the p-type ZnSe epilayers was determined by rf induction at 500 MHz. The series resonant circuit, adapted from NMR technology, includes a $\lambda/2$ section of coaxial cable for convenient access to the tuning element. A 20 dB splitter separates the incoming from the reflected signal. The imbalance in the circuit, monitoring the conductance, is phase detected by a wide dynamic range double balanced mixer (DBM) and then digitized.
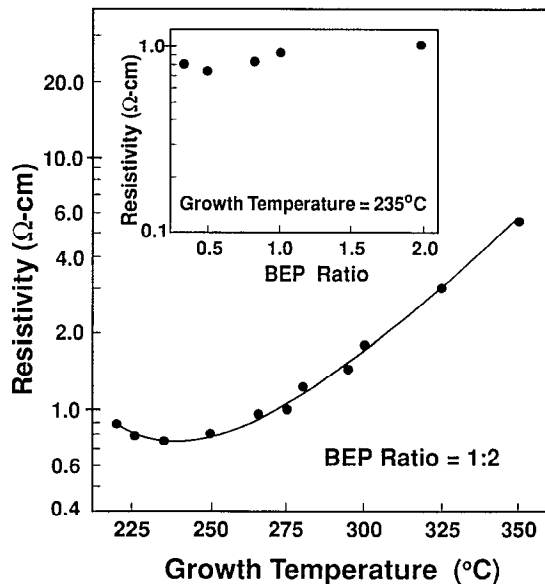

FIG. 2. Growth parameter dependence of the resistivity of p-type ZnSe:N/GaAs epilayers grown by molecular beam epitaxy using a nitrogen free-radical source. A minimum resistivity value of 0.75 Ω cm is indicated for a substrate temperature of 235 °C and a Zn-to-Se beam equivalent pressure (BEP) ratio of 1:2.

the sheet conductance of the sample. To convert this signal to reciprocal ohms or "mhos," it is merely necessary to calibrate the rf bridge against known sheet resistance standards. A tiny background signal due to the substrate dielectric constant was nulled out by using a dummy semi-insulating GaAs substrate. Only the conducting ZnSe layer contributed to the signal, as these layers were grown on semi-insulating GaAs substrates, and extreme care was taken to remove all traces of the In solder that was used to mount the substrates for MBE growth. It should also be noted that in each case, a 0.5-μm-thick unintentionally doped ZnSe buffer layer was grown to isolate the p-type doped ZnSe layers from the GaAs substrate material. The presence of the unintentionally doped, highly resistive ZnSe buffer layer was found to be inconsequential with respect to the reflected rf signal as evidenced by examining undoped ZnSe epilayer/GaAs substrate samples in the apparatus. It is also worth noting that there was no evidence in this case of a conducting layer associated with an undoped ZnSe/GaAs heterointerface.

Resistivity data (obtained by dividing the measured sheet conductivity by film thickness) is plotted in Fig. 2 as a function of both growth temperature (in the range 220 °C to 350 °C) and Zn-to-Se BEP ratio (over the range 1:3 to 1:0.5) for a fixed substrate temperature of 235 °C. It should be noted that layers grown at substrate temperatures of 200 °C and 375 °C were highly resistive. As can be seen from Fig. 2, sample resistivity is strongly dependent on growth temperature while only weakly dependent on Zn-to-Se BEP ratio at the growth temperature of 235 °C. For the conditions investigated, a minimum resistivity of 0.75 Ω cm was obtained for layers grown at a substrate temperature of 235 °C and a Zn-to-Se BEP ratio of 1:2. Such a resistivity would imply a free-hole density in this material in the range of 4×10^{17} to 8×10^{17} cm^{-3} assuming the hole mobility to be in the range 20–10 cm^2 V^{-1} s^{-1}, respectively.

The significant dependence of ZnSe:N layer resistivity on growth temperature can be explained based on an "intrinsic compensation" model. Intrinsic compensation is taken here to mean compensation that results due to the production of point defects as a consequence of growing nonstoichiometric ZnSe material. Since the kinetic processes involved in the MBE growth of ZnSe are very much temperature dependent, point defect production will consequently be strongly temperature dependent. It is likely, for instance, that at relatively high substrate temperatures, Se vacancies will result due to the greater volatility of Se compared to Zn at such temperatures leading to point defect production. At relatively low substrate temperatures a likely cause of defect production would be associated with the inefficient dissociation of incident Se molecules, for example. Such intrinsic (stoichiometric) defects, of course, also pertain to unintentionally doped ZnSe material grown under, so-called, nonoptimum conditions. A second level of compensation will occur in the nitrogen-doped ZnSe layers even for material grown under "optimum" conditions, i.e., growth conditions that result in low intrinsic point defect concentrations. The second level of compensation is the, so-called, self-compensation phenomenon that results as a consequence of the incorporation of the nitrogen impurities (see, for example, Ref. 5). Self-compensation is evidenced by the presence of strong donor-to-acceptor pair (DAP) transition peaks in the photoluminescence spectra recorded from ZnSe:N material (see, for example, Ref. 1). Another issue to consider with regard to ZnSe:N is the depth of the N level in the ZnSe band gap ($\sim$110 meV above the valence band edge). As pointed out by Ruda,[8] only a fraction of the total nitrogen content in ZnSe will be ionized at room temperature. In fact, in order to have a free-hole density in ZnSe:N material of 1×10^{18}

cm^{-3}, a total N concentration in the 10^{19} cm^{-3} range would be necessary. Self-compensation would further reduce the free-hole density below 1×10^{18} cm^{-3} in this example.

Consequently, in view of the above discussion, the minimum resistivity value derived in this work through the performance of an optimization study is probably close to the fundamental limit for ZnSe:N material. Ultimately, the substitutional solid solubility limit of N in ZnSe (probably in the 10^{19} cm^{-3} range for the nonequilibrium MBE growth technique) and self-compensation (possibly through a lattice relaxation process) will determine the maximum free-hole density achievable in stoichiometric ZnSe:N material.

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